

(19) Japanese Patent Office (JP)

(11) Publication Number: 5-113572

(43) Date of publication of application: May 7, 1993

(12) Patent Laid-open Official Gazette (A)

(51) Int. Cl. ⁵

G 02 F 1/1343

1/1335

The Number of Claims: 4 (9 pages in total)

Request of Examination: not made

(21) Application number: Hei3-301070

(22) Filing Date: October 21, 1991

(71) Applicant: 000006747

Ricoh Company, Ltd.

3-6, Nakamagome 1-chome, Ota-ku, Tokyo, Japan

(72) Inventor: Yuji KIMURA

c/o Ricoh Company, Ltd.

3-6, Nakamagome 1-chome, Ota-ku, Tokyo, Japan

(72) Inventor: Hidekazu OTA

c/o Ricoh Company, Ltd.

3-6, Nakamagome 1-chome, Ota-ku, Tokyo, Japan

(72) Inventor: Hitoshi KONDO

c/o Ricoh Company, Ltd.

3-6, Nakamagome 1-chome, Ota-ku, Tokyo, Japan

(74) Representatives: Patent attorney:

Eiji TOMOMATSU

(54) Title of the Invention: COLOR LIQUID CRYSTAL DISPLAY DEVICE

(57) [Abstract]

[Purpose]

To lower the wiring resistance of a transparent pixel electrode as much as possible by forming a portion which is not required to be transparent in the pixel electrode to be a

conductive electrode such as a metal, and to shorten steps by commonly using the conductive electrode as a black mask.

[Constitution]

A liquid crystal display device characterized in that a portion which is not required to be a transparent in a pixel electrode is to be a conductive electrode such as a metal in a color liquid crystal display device with a liquid crystal layer interposed between a pair of transparent substrates.

[Scope of Claims]

[Claim 1]

A color liquid crystal display device characterized by comprising:

a liquid crystal layer interposed between a pair of transparent substrates; and a color filter at least on one substrate,

wherein a color filter, a common conductive electrode, an interlayer transparent insulating layer, and a transparent electrode for display are sequentially formed on a substrate on a side having the transparent electrode for display; and

the common conductive electrode and the transparent electrode for display are connected through a through-hole provided in the interlayer transparent insulating layer.

[Claim 2]

The color liquid crystal display device according to claim 1, characterized in that:

a metal wiring is provided on a portion other than a display region of the transparent electrode for display so as to be the common conductive electrode.

[Claim 3]

The color liquid crystal display device according to claim 1 or 2, characterized in that:

the common conductive electrode is a black mask.

[Claim 4]

The color liquid crystal display device according to claim 1, 2 or 3, characterized in that:

at least one active electrode is provided in each pixel on an opposite substrate of the substrate having the transparent electrode for display.

[Detailed Description of the Invention]

[0001]

[Technical Field]

The present invention relates to a color liquid crystal display device.

[0002]

[Prior Art]

Even ITO which is considered the lowest in resistance among conventional transparent conductive films, the resistivity thereof is about $1 \times 10^{-4} \Omega \cdot \text{cm}$ which is one digit larger compared to a metal material used for a wiring material, and thus the resistivity is extremely large. Therefore, when a display area in a display device is large, delay of a signal and voltage drop are generated due to wiring resistance to cause variations in a display. Heretofore, in an active matrix, an active element side provided on a substrate side opposite to a substrate having a transparent electrode for display has been performed by a metal, and has been performed that the wirings are multilayered to lower wiring resistance and suppress a delay of an input signal. However, wiring resistance on an opposite substrate side, that is, on a side having a transparent electrode for display has not been lowered. Furthermore, for lowering resistance of a wiring on a larger area in a passive matrix, various modifications of an ITO film which is a transparent conductive film has been tested. However, satisfying results have not been obtained yet. In any case, in the prior art, a technique is to multilayer an obscure metal wiring on an active electrode side, there has not been any idea to lower resistance of a transparent electrode for display over an opposite substrate.

[0003]

[Object]

An object of the invention is to obtain stable display even when an area is large and a duty is high in a color liquid crystal display device, by lowering wiring resistance related to a transparent electrode for display as low as possible. Another object of the invention is to shorten a step by using both a wiring and a black mask.

[0004]

[Structure]

A first characteristic of the invention is that a color liquid crystal display device includes a liquid crystal layer interposed between a pair of transparent substrates, and a color filter at least on one substrate, in which a wiring portion of a substrate on a side having a transparent electrode for display is a conductor such as a metal material, by using a transparent electrode only for a display portion to solve the problem of the prior art. That is, the color liquid crystal display device is characterized in that a color filter and a common conductive electrode are formed over the substrate, a transparent interlayer insulating layer is formed over the color filter and the common conductive electrode, further, a transparent electrode for display is formed over the transparent interlayer insulating layer and the common conductive electrode and the transparent electrode for display are connected through a through-hole provided in the transparent interlayer insulating layer as a substrate structure on a side having the transparent electrode for display. A second characteristic of the invention is characterized in that the common conductive electrode is also used for a black mask in the color liquid crystal display device.

[0005]

Next, description is made on a structure on a substrate side having the color filter and an electrode for display, used for a liquid crystal display device of the invention, and a manufacturing method thereof with reference to FIG. 7. However, the structure and the manufacturing method are not limited to FIG. 7 and the following manufacturing method. First, a glass plate, a plastic plate, a flexible plastic film, or the like is used for an insulating transparent substrate 1. First, over these transparent substrates 1, a metal material such as Al, Cr, Ni, Pt, Ta, Ti, Mo, W, Cu, Ag, and Au is deposited with a thickness of several hundreds Å to several μm by a sputtering method, a vapor deposition method, a CVD method, and the like, then patterned into a predetermined pattern to provide a common conductive electrode 14. Subsequently, a color filter 12 is provided by an appropriate means such as a printing method, a resist method, and an electrodeposition process. One example of the color filter 12 arrangement is, for example, shown in FIG. 8. A transparent interlayer insulating layer 15 is provided over the color filter and the common conductive electrode 14. In the insulating layer 15, a through-hole connecting a transparent electrode 13 for display formed thereover and the common conductive

electrode 14 is provided, and the transparent electrode 13 for display is formed over the insulating layer 15 to connect the both electrodes through the through-hole. Photosensitive polymer such as polyimide, polyester, and an epoxy resin can be synthesized at a low temperature (UV irradiation), in addition, a photolithography step can be omitted because of patterning. Subsequently, as a transparent pixel electrode, materials such as ITO, ZnO:Al, ZnO:Si, and SnO₂:Sb are deposited with a thickness of several hundreds Å to several μm by the sputtering method, the vapor deposition method, the CVD method, and the like, then patterned into a predetermined pattern. As the transparent interlayer insulating layer 15, a hard carbon film, SiN_x, SiO₂, SiO_x, Si₃N₄, Al₂O₃, polyimide, polyester, an epoxy resin, polyamide, PVDC, PVDF, PVA, a silicon resin, fluorocarbon, and the like are manufactured by the CVD method, the sputtering method, the vapor deposition method, a coating method (spin coating, roll coating, and the like) and the like.

[0006]

Conventionally, in a color display device, a black mask is manufactured in a portion which does not display between pixels to reduce leak light and improve contrast display quality. However, the conductor is not a transparent material according to the invention, therefore, a portion in which the conductor exists does not transmit light. Therefore, the portion can function as a black mask, thereby when a metal wiring is patterned into a black mask of a color filter, a black mask is not required to be manufactured and a color liquid crystal display device capable of sharp display can be manufactured. As a pattern in this case, for example, there are FIGS. 8(a), 8(b), and 8(c) as well as various arrangement methods. In the drawings, denoted are three primary colors in which B denotes blue, R denotes red, and G denotes green. In an active matrix display method capable of high brilliance and a high duty with a duty ratio of 1/400 or higher, selection time per pixel is short and input signal width shortens since gray scale display is performed, thereby there is a problem in that an input signal delays. In addition, there is a big problem of high resistivity of wiring resistance due to a large area. For this measure, in which wirings on an active element side are formed of a stacked layer of metal wirings so as to have lower resistance. However, the delay of an input signal due to high

resistance on a transparent electrode for display side on an opposite substrate side, and voltage drop can unavoidable, therefore, the invention plays a great role.

[0007]

A color liquid crystal display device of the invention is manufactured using the substrate having the color filter and the electrode for display and the substrate provided with an active element such as a TFT and an MIM per each pixel as an opposite substrate. Subsequently, description is specifically made on a method for manufacturing a color liquid crystal display device of the invention. FIG. 1 is a fragmentary perspective view of a liquid crystal display device of the invention. First, a glass plate, a plastic plate, a flexible plastic film, or the like is used for the insulating transparent substrate 1. As a transparent electrode material for liquid crystal display, a transparent electrode material such as ITO, ZnO:Al, ZnO:Si, and SnO₂:Sb is deposited over the substrate with a thickness of several hundreds Å to several μm by the sputtering method, the vapor deposition method, the CVD method, and the like, then patterned into a predetermined pattern. A transparent electrode is patterned, thereafter, an active element (switching element) 5 and a common electrode 6 are provided in each pixel electrode 4 to make an active matrix substrate. A TFT element using such as a-Si and Poly-Si is used for the active element 5 while a hard carbon film, an MIM element, an MSI element, a PIN diode, a back-to-back diode, and a varistor using such as SiN_x, SiC, Ta₂O₅, Al₂O₃, and the like are used for an insulating layer, and the like. The above used transparent electrode materials and a high conductive material such as Al, Ni, Cr, Ni-Cr, Mo, Ta, Ti, Au, Ag, and Pt is used for a common electrode wiring to be deposited with a thickness of several hundreds Å to several μm by the sputtering method, the vapor deposition method, the CVD method, and the like, and then patterned. In this manner, an active matrix substrate is obtained. The transparent substrate 1 having the aforementioned color filter 12 is used for an opposite substrate 1 of these substrates and an oriented material 8 such as polyimide is applied to the surface thereof, rubbing treatment is performed, a sealing material is provided, a gap material 9 is introduced to keep a gap constant, and a liquid crystal 3 is sealed to form a liquid crystal display device. Note that although there are a three-terminal element such as a TFT and a two-terminal element such as a conductor-insulator-conductor (MIM)

element as for the aforementioned active element, the MIM element is advantageous in the structure and the easy manufacturing method. Specifically, in the case where a hard carbon film is used for an insulating layer of an MIM element, it is in particular desirable since a liquid crystal display device can be manufactured with large area, less defect and high quality by a method for manufacturing the hard carbon film and film quality.

[0008]

Description is made in details on a method for manufacturing an MIM type element used in the invention with reference to FIG. 2. First, a transparent electrode material for pixel electrode is deposited over the transparent insulating substrate 1 such as glass, a plastic plate, and a plastic film by the sputtering method and the like, and then patterned into a predetermined pattern to form the pixel electrode 4. Subsequently, a conductive thin film for lower electrode is formed by the vapor deposition method, the sputtering method and the like, patterned into a predetermined pattern by wet etching or dry etching to form a first conductor 7 to be a lower electrode, and then a hard carbon film 2 is covered thereover by a plasma CVD method, an ion beam method and the like, thereafter patterned into a predetermined pattern by dry etching, wet etching, a lift-off method using a resist to form an insulating film. Subsequently, a conductive thin film for bus line is covered thereover by the vapor deposition method, the sputtering and the like, patterned into a predetermined pattern to form the second conductor 6 to be a bus line. At last, an unnecessary portion of a lower electrode 7 is removed to expose a transparent electrode pattern to form the pixel electrode 4. In this case, a structure of an MIM element is not limited to this, and various modification can be made such as a structure in which a transparent electrode is provided over the uppermost layer after forming an MIM element, a structure in which a transparent electrode functions as an upper electrode or a lower electrode, and a structure in which an MIM element is formed on a side of a lower electrode.

[0009]

Here, thicknesses of the lower electrode, the common electrode, and the transparent electrode are normally in the ranges from several hundreds to several thousands Å, from several hundreds to several thousands Å, and from several hundreds to several

thousands Å respectively. A thickness of the hard carbon film is in a range from 100 to 8000 Å, desirably 200 to 6000 Å, and more desirably 300 to 4000 Å. Further, in the case of a plastic substrate, it was very hard to manufacture an active matrix device using an active element because of the heat resistance so far. However, a hard carbon film can be manufactured favorably at a substrate temperature at about a room temperature, and can also be manufactured over a plastic substrate, therefore, the hard carbon film is very effective for improving image quality.

[0010]

Next, description is made in further details on a material of an MIM element used in the invention. As a material of the first conductor 7 to be a lower electrode, various conductors such as Al, Ta, Cr, W, Mo, Pt, Ni, Ti, Cu, Au, W, ITO, ZnO:Al, In₂O₃, and SnO₂ are used. Next, as a material of the second conductor 6 to be a bus line, various conductors such as Al, Cr, Ni, Mo, Pt, Ag, Ti, Cu, Au, W, Ta, ITO, ZnO:Al, In₂O₃, and SnO₂ are used. However, in the regard that the stability of I-V characteristics and reliability are specifically excellent, Ni, Pt, and Ag are preferable. In the MIM element in which the hard carbon film 2 is used for an insulating film, it turns out that symmetry does not change even when kinds of electrodes are changed, and the Poole-Frenkel conduction is taken according to $\ln I \propto \sqrt{V}$. Accordingly, in the case of such kinds of MIM elements, it turns out that the upper electrode and the lower electrode may be used in any combination. However, a deterioration and a change of element characteristics (I-V characteristics) occur due to an interface state and an adhesion force between the hard carbon film and an electrode. In consideration of these, it turns out that Ni, Pt, and Ag are favorably used. A current-voltage characteristic of the MIM element of the invention is expressed as shown in FIG. 4, and approximately described by conductive equations shown as follows.

[Equation 1]

$$I = \kappa \exp\left(\beta V^{\frac{1}{2}}\right) \dots (1)$$

$$\kappa = \frac{n\mu q}{d} \exp\left(\frac{-\Phi}{kT}\right) \propto \frac{1}{\rho d} (T = \text{constant}) \dots (2)$$

$$\beta = \frac{1}{kT} \left(\frac{q^3}{\pi \epsilon_1 \epsilon_2 d} \right)^{\frac{1}{2}} \propto \frac{1}{\sqrt{\epsilon_2 d}} (T = \text{constant}) \dots (3)$$

I : current V : applied voltage κ : conductive coefficient β : Poole-Frenkel coefficient

n : carrier density μ : carrier mobility q : electron charge amount F : trap depth

ρ : resistivity d : thickness of hard carbon (Å) k : Boltzmann constant T : atmosphere temperature

ϵ_1 : dielectric constant of hard carbon ϵ_2 : dielectric constant of vacuum

This MIM element is suitably applied to a switching element of a liquid crystal display device.

[0011]

Description is made in details on a hard carbon film of the invention. An organic compound gas, specifically a hydrocarbon gas is used for forming a hard carbon film. A phase condition of these materials is not necessarily a vapor phase at a normal temperature and normal pressure. Therefore, when the material can be evaporated by heating, reducing pressure, or the like through melting, evaporation, sublimation, and the like, a liquid phase or a solid phase can be used. As a hydrocarbon gas as a source gas, a gas including at least all hydrocarbon, for example, paraffinic hydrocarbon such as CH₄, C₂H₆, C₃H₈, and C₄H₁₀, olefinic hydrocarbon such as C₂H₄, acetylenic hydrocarbon, diolefin-based hydrocarbon, further, aromatic hydrocarbon, and the like can be used. Moreover, other than hydrocarbon, a compound including at least hydrocarbon, for example, alcohols, ketones, ethers, esters, CO, CO₂ and the like can be used. As a method for forming a hard carbon film from the source gas in the invention, a method is preferable in which deposition active species are formed through a plasma state generated

by a plasma method using direct current, low frequency, high frequency, a microwave, or the like. However, deposition is performed under low pressure for the purpose of further enlarging area, improving uniformity, and depositing at a low temperature. Therefore, a method using a magnetic field effect is more preferable. Moreover, active species can be formed by thermal decomposition at a high temperature. In addition, active species may be formed through an ion state generated by an ion vapor deposition method, an ion beam vapor deposition method, or the like, and may be formed by a neutral particle generated by a vacuum vapor deposition method, the sputtering method, or the like. Furthermore, active species may be formed by combining them. In the case of the plasma CVD method, one example of a deposition condition of a hard carbon film manufactured in this manner is as follows.

RF output : 0.1 to 50 W/cm²

Pressure : 1/10³ to 10 Torr

Deposition temperature : room temperature to 950°C

The source gas is divided into radical and ion to react by this plasma state, therefore, a hard carbon film including at least one of amorphous (amorphous) including carbon atom C and hydrogen atom H over a substrate and microcrystal (a size of grain is several 10 Å to several μm) thereover is deposited. Note that various characteristics of the hard carbon film are shown in Table 1.

[Table 1]

Resistivity (ρ)	10 ⁶ to 10 ¹³ Ωcm
Optical band gap (E _g)	1.0 to 3.0 eV
Amount of hydrogen in a film [C (H)]	10 to 50 atm%
Ratio of SP ³ /SP ²	2/1 to 4/1
Vickers hardness (H)	9500 kg/mm ² or less
Refractive index (n)	1.9 to 2.4
Defect density	10 ¹⁷ to 10 ¹⁹ /cm ³

Resistivity (ρ) : obtained by I-V characteristics of a coplanar cell.

Optical band gap (E_{gopt}) : determined according to absorption coefficient (α) obtained by spectral characteristics and according to Equation 2.

[Equation 2]

$$(\alpha h\nu)^{\frac{1}{2}} = B(h\nu - E_{\text{gopt}})$$

Amount of hydrogen in a film [C (H)] : obtained by integrating a peak in the vicinity of 2900 /cm of an infrared absorption spectrum and multiplying by an absorption cross section area A. That is,

$$C(H) = A \cdot \int a(\nu) / \nu \cdot d\nu$$

Ratio of SP^3/SP^2 : obtained by dividing an infrared absorption spectrum into a Gaussian function to which each of the SP^3 and the SP^2 belongs, and obtaining the area ratio.

Vickers hardness (H) : by micro Vickers measurement.

Refractive index (n) : by ellipsometer.

Defect density : by ESR.

In this manner, as an analysis result by Raman spectroscopy and IR absorption spectrometry, it is revealed that an interatomic bond in which an SP^3 hybrid orbital and an SP^2 hybrid orbital are formed in a carbon atom coexists in the carbon atom as shown in FIGS. 4 and 5 in the hard carbon film formed in this manner. A ratio of SP^3 bond and SP^2 bond is approximately estimated by a peak-separation of IR spectrum. The IR spectrum is measured by overlapping many mode spectra in 2800 to 3150 /cm, however, each peak assignment corresponding to wavenumber is revealed. Therefore, the peak-separation is performed by a Gaussian distribution as FIG. 6, each peak area is calculated, and the ratio thereof is obtained to know SP^3/SP^2 . Moreover, according to an X-ray analysis and an electron diffraction analysis, it is turned out that the hard carbon film is on an amorphous state (a-C : H), and/or an amorphous state containing a microcrystal grain with a grain size approximately about 50 Å to several μm. In general, in the case of the plasma CVD

method suitable for mass production, when an RF output is small, resistivity and hardness of a film increase, while when pressure is low, a substrate temperature is lowered and uniformity in a large area is achieved, and resistivity and hardness tend to increase since life of active species increases. In addition, plasma density decreases with low pressure, therefore, a method using an effect of magnetic confinement is particularly effective for increasing resistivity. Furthermore, this method has a characteristic that a good quality hard carbon film can be formed similarly even when at a relatively low temperature condition about a room temperature to 150°C, therefore, this method is the most favorable to lower temperature of an MIM element manufacturing process. Accordingly, the degree of freedom in selection of a substrate material to use expands and a uniform film can be obtained in a large area since a substrate temperature is easy to control. Further, as shown in Table 1, a structure and a physical property of a hard carbon film can be controlled in a wide range, therefore, there is an advantage in that device characteristics can be freely designed. Furthermore, a dielectric constant of a film is also as small as 3 to 5 compared to Ta₂O₅, Al₂O₃, and SiN_x which are conventionally used for an MIM element. Therefore, in the case of making an element having the same capacitance, an element size may be large so that microfabrication is not required so much and yield is employed (according to a driver condition, a capacity ratio of an LCD and an MIM element is required to be about $C(\text{LCD}) : C(\text{MIM}) = 10 : 1$). Further, steepness of an element is $\beta \propto 1 / v_e \cdot v_d$, therefore, when the dielectric constant ϵ is small, steepness increases, thereby a larger ratio of an on current I_{on} and an off current I_{off} can be obtained. Therefore, an LCD drive with low duty ratio is possible to realize an LCD with high density. Moreover, as film density is high, damage by a rubbing step when a liquid crystal material is encapsulated is small. The yield is improved in this respect as well. In view of the aforementioned points, a hard carbon film is used so that low cost, gray scale property (colorization), a high density LCD, and the like can be realized. Furthermore, this hard carbon film may include as a structural element a carbon atom and a hydrogen atom as well as an element belonging to group III of the periodic table, an element belonging to group IV thereof, an element belonging to group V thereof, an alkaline metal element, an alkaline earth metal element, a nitrogen atom, an oxygen atom, a chalcogen-based element, or a halogen atom.

As one of the structural elements, a hard carbon film to which the element belonging to group III of the periodic table, the element belonging to group V thereof, the alkaline metal element, the alkaline earth metal element, the nitrogen atom or the oxygen atom is introduced can be formed about 2 or 3 times as thick compared to a non-doped hard carbon film. Therefore, when manufacturing an element, a pin-hole can be prevented from generating as well as a mechanical strength of an element can be improved dramatically. In addition, in the case of the nitrogen atom or the oxygen atom, there is a similar effect as the case of the element belonging to group IV of the periodic table and the like as described below. Similarly, stability of a hard carbon film to which the element belonging to group IV of the periodic table element, the chalcogen-based element, or the halogen element is introduced can be improved dramatically as well as an element with high reliability can be manufactured with improved film hardness. These effects are obtained because in the case of the element belonging to group IV and the chalcogen-based element, active dangling bonds existing in a hard carbon film is reduced. In the case of the halogen element, 1) a source gas is promoted to be divided by abstraction reaction against hydrogen to reduce dangling bonds in the film, 2) in a deposition process, a halogen element X extracts hydrogen in a C-H bond, and substitutes it, enters into a film as a C-X bond and increases bond energy (bond energy between C-X is larger than that between C-H). To make these elements as a film structural element, a compound (or molecule) gas (hereinafter also referred to them as "other compound") including these elements and atoms is used in order to include a carbon hydrogen gas and hydrogen as well as the element belonging to group III of the periodic table, the element belonging to group IV thereof, the element belonging to group V thereof, the alkaline metal element, the alkaline earth metal element, the nitrogen atom, the oxygen atom, the chalcogen system element, or the halogen element in a film as a source gas. Here, as a compound including the element belonging to group III of the periodic table, there are, for example, $\text{B}(\text{OC}_2\text{H}_5)_3$, B_2H_6 , BCl_3 , BBr_3 , BF_3 , $\text{Al}(\text{O}-i\text{-C}_3\text{H}_7)_3$, $(\text{CH}_3)_3\text{Al}$, $(\text{C}_2\text{H}_5)_3\text{Al}$, $(i\text{-C}_4\text{H}_9)_3\text{Al}$, AlCl_3 , $\text{Ga}(\text{O}-i\text{-C}_3\text{H}_7)_3$, $(\text{CH}_3)_3\text{Ga}$, $(\text{C}_2\text{H}_5)_3\text{Ga}$, GaCl_3 , GaBr_3 , $(\text{O}-i\text{-C}_3\text{H}_7)_3\text{In}$, $(\text{C}_2\text{H}_5)_3\text{In}$, and the like. As a compound including the element belonging to group IV of the periodic table, there are, for example, Si_3H_6 , $(\text{C}_2\text{H}_5)_3\text{SiH}$, SiF_4 , SiH_2Cl_2 , SiCl_4 , $\text{Si}(\text{OCH}_3)_4$, $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Si}(\text{OC}_3\text{H}_7)_4$,

GeCl₄, GeH₄, Ge(OC₂H₅)₄, Ge(C₂H₅)₄, (CH₃)₄Sn, (C₂H₅)₄Sn, SnCl₄, and the like. As a compound including the element belonging to group V of the periodic table, there are, for example, PH₃, PF₃, PF₅, PCl₂F₃, PCl₃, PCl₂F, PBr₃, PO(OCH₃)₃, P(C₂H₅)₃, POCl₃, AsH₃, AsCl₃, AsBr₃, AsF₃, AsF₅, AsCl₃, SbH₃, SbF₃, SbCl₃, Sb(OC₂H₅)₃, and the like. As a compound including the alkaline metal atom, there are, for example, LiO-i-C₃H₇, NaO-i-C₃H₇, KO-i-C₃H₇, and the like. As a compound including the alkaline earth metal atom, there are, for example, Ca(OC₂H₅)₃, Mg(OC₂H₅)₂, (C₂H₅)₂Mg, and the like. As a compound including the nitrogen atom, there are, for example, an inorganic compound such as a nitrogen gas and ammonia, an organic compound having a functional group such as an amino group and a cyano group, a heterocycle including nitrogen, and the like. As a compound including the oxygen atom, for example, an inorganic compound such as an oxygen gas, ozone, water (moisture), hydrogen peroxide, carbon monoxide, carbon dioxide, carbon suboxide, nitric monoxide, nitrogen dioxide, dinitrogen trioxide, dinitrogen pentoxide, nitrogen trioxide, a functional group such as a hydroxyl group, an aldehyde group, an acyl group, a ketone group, a nitro group, a nitroso group, a sulfone group, an ether bond, an ester bond, a peptide bond, and a heterocycle including oxygen, an organic compound including a bond, metal alkoxide, or the like. As a compound including the chalcogen system element, there are, for example, H₂S, (CH₃)(CH₂)₄S(CH₂)₄CH₃, CH₂=CHCH₂SCH₂CH=CH₂, C₂H₅SC₂H₅, C₂H₅SCH₃, thiophene, H₂Se, (C₂H₅)₂Se, H₂Te, and the like. Moreover, as a compound including the halogen element, for example, an inorganic compound such as fluorine, chlorine, bromine, iodine, hydrogen fluoride, chlorine fluoride, bromine fluoride, iodine fluoride, hydrogen chloride, bromine chloride, iodine chloride, hydrogen bromide, iodine bromide, hydrogen iodide, and an organic compound such as alkyl halide, aryl halide, styrene halide, polymethylene halide, and haloform is used.

[0012]

[Embodiment]

Embodiment 1

An embodiment is described below. However, the invention is not limited to this. A Pyrex substrate is used for a transparent substrate, then ITO is deposited using an 800 Å

magnetron sputtering method, and then patterned to form a pixel electrode. Subsequently, an MIM element using a hard carbon film for an active element is provided as follows. First, Al is deposited with a thickness of 800 Å by the vapor deposition method over the pixel electrode of the substrate, thereafter patterned to form a lower electrode. A hard carbon film is deposited with a thickness of 900 Å by the plasma CVD method thereover as an insulating film, thereafter patterned by dry etching. Further, Ni is deposited with a thickness of 1000 Å by the vapor deposition method over each hard carbon insulating film, thereafter patterned to form an upper electrode. As an opposite substrate, Al is deposited with a thickness of 5000 Å over the Pyrex substrate and patterned to be a common wiring and a black mask. Subsequently, color filters of R, G, and B are manufactured by the resist method. Subsequently, an epoxy resin is applied, and then a through-hole is formed. Subsequently, ITO is deposited with a thickness of 1000 Å and patterned into a predetermined pattern to be a substrate with a color filter. Subsequently, a polyimide film is formed over these substrates as an alignment film and rubbing treatment is applied. Subsequently, these substrates are opposed to each other with each pixel electrode side set inside, attached to each other with a gap material interposed therebetween, and a liquid crystal material is encapsulated in a cell formed in this manner to form a color liquid crystal display device. At this time, deposition conditions of hard carbon used for the MIM element are

Pressure : 0.03 Torr

Flow rate of CH₄ : 10 SCCM

RF power : 0.2 W/cm²

Temperature : room temperature.

Embodiment 2

A plastic substrate is used for a transparent substrate and SiO_x is coated over both sides of the substrate with a thickness of 4000 Å, then ITO is deposited using a 1000 Å magnetron sputtering method, then patterned to form a pixel electrode. Subsequently, an MIM element using a hard carbon film as an active element is provided as follows. First, Al is deposited with a thickness of 600 Å by the vapor deposition method over the pixel

electrode of the substrate, thereafter patterned to form a lower electrode. A hard carbon film is deposited with a thickness of 1100 Å by the plasma CVD method thereover as an insulating film, thereafter patterned by dry etching. Further, Ni is deposited with a thickness of 1000 Å by the vapor deposition method over each hard carbon insulating film, thereafter patterned to form an upper electrode, then Cr is deposited with a thickness of 1 μm over a flexible plastic film substrate as a substrate with a color filter, then patterned into a predetermined pattern to be a common electrode and a black mask. Subsequently, a color filter is manufactured by the printing method. Subsequently, a polyimide film is provided as an interlayer insulating layer, then a through-hole is manufactured. Subsequently, ITO is deposited thereover and patterned to be a pixel electrode. Subsequently, a polyimide film is formed over both substrates as an alignment film and rubbing treatment is performed. Subsequently, these substrates are opposed to each other with each pixel electrode side set inside, attached to each other with a gap material interposed therebetween, and a liquid crystal material on the market is encapsulated in a cell formed in this manner to form a color liquid crystal display device. At this time, deposition conditions of the hard carbon used for the MIM element are

Pressure : 0.05 Torr

Flow rate of CH₄ : 10 SCCM

RF power : 0.3 W/cm²

Temperature : room temperature.

Embodiment 3

An MIM element is provided over a Pyrex glass substrate as one transparent substrate as follows. Cr is deposited with a thickness of 1000 Å by the sputtering method, thereafter patterned to form a lower common electrode. Subsequently, a SiN_x film is formed with a thickness of 800 Å thereover by a P-CVD method using SiH₄ and NH₃, thereafter patterned to form an insulating film. Further, Cr is deposited with a thickness of 2000 Å thereover, thereafter patterned to be an upper electrode. Subsequently, ITO is deposited with a thickness of 500 Å over the MIM element formed in this manner by the sputtering method and patterned to be a pixel electrode. Subsequently, Ta is deposited

with a thickness of 8000 Å over a Pyrex substrate as a substrate with a color filter and patterned to be a common electrode and a black stripe. Subsequently, a color filter is manufactured by the printing method. Subsequently, SiO₂ is manufactured with a thickness of 1 μm as an interlayer insulating layer, then a through-hole is provided. ITO is deposited thereover and patterned to be a pixel electrode. Subsequently, these substrates are opposed to each other with each pixel electrode side set inside, attached to each other with a gap material interposed therebetween, and a liquid crystal material is encapsulated in a cell formed in this manner to form a color liquid crystal display device. Subsequently, a polyimide film is formed over all substrates as an alignment film and rubbing treatment is performed.

Embodiment 4

A TFT as an active element is formed over a quartz substrate as one transparent substrate. The forming method is as follows. First, a poly-Si active layer is deposited with a thickness of 2000 Å by a low pressure CVD method over a substrate at a substrate temperature of 850°C, then a gate insulating film composed of SiO₂ is formed thereover with a thickness of 3000 Å, then a gate electrode composed of poly-Si is formed thereover with a thickness of 1000 Å, and then Al is deposited thereover with a thickness of 3000 Å to form a source/drain electrode. A SiO₂ film is formed with a thickness of 8000 Å as interlayer insulating layer. Diffusion of an impurity element to the poly-Si active layer is performed using an impurity diffusion material of applying system, however, a method by an ion injection and the like is also possible. Other steps are similarly performed to Embodiment 1 to obtain a color liquid crystal display device.

Embodiment 5

First, Cr is deposited with a thickness of 6000 Å over a Pyrex substrate and patterned into a predetermined pattern. Subsequently, a color filter is manufactured by the resist method. Subsequently, polyester is provided with a thickness of 2 μm as an interlayer insulating layer to manufacture a contact hole therein. ITO is deposited thereover and patterned into a predetermined pattern to be a pixel electrode.

Subsequently, ITO is deposited with a thickness of 1000 Å by the sputtering method over the Pyrex substrate as the other transparent substrate, thereafter patterned into a stripe shape to be a common pixel electrode. Subsequently, a polyimide film is formed over these substrates as an alignment film and rubbing treatment is performed. Subsequently, these substrates are opposed to each other with each pixel electrode side set inside, attached to each other with a gap material interposed therebetween, and a liquid crystal material is encapsulated in a cell formed in this manner to form a color liquid crystal display device.

[0013]

[Effect]

In the invention, a portion which is not required to be transparent in the transparent electrode is to be a conductive electrode similar to a metal, (1) wiring resistance decreases, signal delay and voltage drop do not occur so that display characteristics improve, (2) a stacked conductive layer becomes a black mask so that wiring resistance decreases and leak light does not occur, therefore a color liquid crystal display device capable of high contrast display can be obtained, (3) in an active matrix display device, high gray scale and high contrast display are possible without a signal delay even in a large area and a high duty.

[Brief Description of the Drawings]

FIG. 1 is a perspective view showing one example of a liquid crystal display device of the invention.

FIG. 2 is a perspective view showing one example of an MIM type element used for the invention.

FIGS. 3a and 3b show a typical I-V characteristic diagram of an MIM element of the invention and a typical $\ln I$ - v characteristic diagram thereof.

FIG. 4 is a spectrum diagram showing an analysis result in which a hard carbon film used for an insulating layer of an MIM type element usable in the invention is analyzed by IR absorption spectrometry.

FIG. 5 is a spectrum diagram showing an analysis result in which a hard carbon film used for an insulating layer of an MIM type element of the invention is dispersed by

Raman spectroscopy.

FIG. 6 is a Gaussian distribution view of IR spectrum.

FIG. 7 shows a substrate structure on a side having a transparent pixel electrode and a color filter of a color liquid crystal display device of the invention.

FIGS. 8a, 8b and 8c show examples each showing an arrangement pattern of B, R, and G of a color liquid crystal display device of the invention.

[Description of the Numerals]

1: insulating substrate, 2: hard carbon film, 3: liquid crystal, 4: pixel electrode, 5: active element, 6: second conductor (bus line) (common electrode), 7: first conductor (lower electrode), 8: alignment film, 9: gap material, 11: substrate, 12: color filter, 13: transparent electrode for display, 14: common conductive electrode, 15: interlayer insulating layer

(72) Inventor: Katsuyuki YAMADA
c/o Ricoh Company, Ltd.
3-6, Nakamagome 1-chome, Ota-ku, Tokyo, Japan

(72) Inventor: Kenji KAMEYAMA
c/o Ricoh Company, Ltd.
3-6, Nakamagome 1-chome, Ota-ku, Tokyo, Japan

(72) Inventor: Masayoshi TAKAHASHI
c/o Ricoh Company, Ltd.
3-6, Nakamagome 1-chome, Ota-ku, Tokyo, Japan

(72) Inventor: Makoto TANABE
c/o Ricoh Company, Ltd.
3-6, Nakamagome 1-chome, Ota-ku, Tokyo, Japan